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External Contamination of Landmines by Organic Nitro-Compounds

Daniel C. Leggett, Thomas F. Jenkins, Austin W. Hogan, Thomas Ranney, and Paul H. Miyares

March 2000

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Abstract: It has been known for years that landmines are contaminated on their surfaces by explosive compounds. Subsequently, it was shown that TNT vapor-contaminated surfaces outgas at a significant rate. This has encouraged the quest for chemical systems for buried mine detection. This report documents a recent study of four types of mines obtained from former Yugoslavian inventories. In addition it presents the results of a study of 18 foreign and domestic types of landmines examined in 1992. Contamination was removed from known areas of the surface by solvent-soaked swabs and several swabs pooled for each mine. Surface concentrations ranged from 1 to 400 ng/cm^2 over all mine types, but was generally less variable within each type. There appears to be an increase of surface contamination with temperature, though this could be due to increased flux rather than increased concentration. Sampling mine casings using swabs may recover more than is truly on the surface, because contamination is regenerated from within material by diffusive permeation. Similarly, single swabs recover this subsurface contamination inefficiently, as sequential sampling of the same area continues to extract contamination. For this reason, these measurements under-represent source size. Surface concentrations are influenced by conditions external to the mines, and after deployment will be influenced by soil moisture.

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PREFACE

This report was prepared by Daniel C. Leggett, Research Chemist, Geochemical Sciences Division, Dr. Thomas F. Jenkins, Research Chemist, Geological Sciences Division, Dr. Austin W. Hogan, CRREL retired, Thomas Ranney, Research Scientist, Science and Technology Corporation, and Dr. Paul H. Miyares, Research Chemist, Geochemical Sciences Division, Cold Regions Research and Engineering Laboratory, U.S. Army Engineer Research and Development Center.

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INTRODUCTION

Chemical sensing of landmines requires a sufficient emission of chemical species into the local environment to form a detectable signature. Mines are externally contaminated in the process of manufacture, primarily during filling operations. U.S. mines are customarily placed in wooden boxes for storage in bunkers. During storage, vapor transport could effectively contaminate all mines in proximity (Bender et al. 1992). A study of 51 bunker-stored landmines of foreign and domestic origin (Hogan et al. 1992) supports this conjecture but doesn't rule out permeation through mine casings as a source of surface contamination. Bender et al. (1992) also demonstrated that painted metal and other materials contaminated with TNT vapor outgas at a significant rate for many days.

PRIOR WORK

In 1992 a joint study by CRREL and Thermedetec, Inc., characterized the surface contamination of 18 mine types of seven national origins, variously encased in metal, plastic, or fiberglass. Surface samples were taken by swabbing a 5-cm^2 area with a cotton swab saturated with acetone. Each mine was swabbed in two different areas, and the individual swabs were analyzed independently using different methods. One set was analyzed for 2,4,6-trinitrotoluene (TNT) and 1,2,5-triazine (RDX) by gas chromatography with a thermal energy analyzer (GC-TEA) at Thermedetec, Inc., Woburn, Massachusetts. These results were reported in the memo by Hogan et al. (1992).

The other set was analyzed at CRREL by high performance liquid chromatography with ultraviolet detection (HPLC-UV). These data are reported here for the first time. Statistical analysis indicates that the data are spatially very heterogeneous and that this is not attributable to systematic differences in laboratory or method. Most of the mines were contaminated with 2,4-dinitrotoluene (2,4-DNT), TNT, and RDX, and less frequently, Tetryl, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), aminodinitrotoluenes, and 1,3,5-trinitrobenzene (TNB). Unfortunately, 1,3-dinitrobenzene was added to all the vials as an internal standard before we realized that it was a prevalent component in some landmine signatures.

Concentrations of the major analytes ranged over many orders of magnitude in the 1992 work (Appendix A). Some mines were very clean—for example, the metallic U.S. M16 antipersonnel mine, in which TNT was detected on only one of eight mines, and in only one of sixteen swabs, as the paired swab was blank as well. Since these M16s were used previously in mine lane trials, they may have been cleaned prior to burial, or burial may have effectively removed surface contamination. Unlike plastic mines, they would not recontaminate by permeation. All the plastic mines examined had detectable surface contamination. The TMA3 was by far the most contaminated. The Humanitarian Demining Database (1999) describes this mine as a block of cast TNT with a thin fiberglass coating. RDX/HMX accounted for more than one-third of the signature, suggesting that what was being sampled by the swab was more like a bulk explosive phase than a deposited vapor; volatility considerations would seem to rule out vapor phase transport of HMX. This quan-

Table 1. Summary of surface concentrations on landmines sampled at the Naval Ordnance Station in 1992 (ng/cm²).

	TNT	*2,4-DNT*	*RDX*
Min.	<2	<2	<2
Max.	540	570	590
Mean	74	32	30
Median	12	<2	7

tity of RDX/HMX also suggests that the explosive was not cast TNT, but a mixture of TNT and RDX such as Composition B. Published information on explosive fills is not always reliable.

Most of the mines contained RDX and TNT, and RDX was found nearly as frequently as TNT in the swabs. Vapor phase transport of RDX seems unlikely because of its low volatility, some 3 orders of magnitude lower than that of TNT, and suggests that contamination arrived on the surface by direct contact. Small amounts of TNT degradation products, TNB and amino-dinitrotoluenes, were often found as well. Measured surface concentrations of the major contaminants on all but the TMA3 (Appendix A) are summarized in Table 1. The detection limit for these analytes was about 2 ng/cm². The data range over 3 orders of magnitude for all contaminants and are highly skewed, with the median value much lower than the mean.

METHODS

Some caveats about swabbing as a method of surface sampling should be given. The original work of Hogan et al. (1992) used commercial cotton swabs (Q-tips) and acetone solvent, which is invasive to paints and plastics. Subsequently, it was shown that serial acetone swabs over the same area of painted metal surfaces continue to extract contamination.* We think this is to be expected, because paint and plastic are three-dimensional reservoirs that can renew their surface contamination by outward permeation; enhanced recovery may also result from inward solvent penetration. Thus, there is always a kinetic aspect owing to transport of signature through the material and to the surface from within. This is especially true of plastics, which are commonly used in casings, but also of painted metal. The rate of explosive permeation through plastics is under investigation and will be reported elsewhere (Leggett and Cragin, in prep.).

This study included surface samples from four types of Yugoslavian landmines. All of the landmines sampled had been in storage for 40–50 years and had never been emplaced. Most of these mines were sampled at Fort Leonard Wood, Missouri, in July of 1998, where the ambient conditions were sunny, hot, and windy. A smaller number were transported to CRREL and sampled under controlled environmental conditions. Paper filter disks, 1.5 cm in diameter, were saturated in methanol and placed randomly over the mine surfaces. Upon drying they were picked up with forceps and transferred to an amber vial containing acetonitrile. Multiple disks were composited to form a single sample. The number of disks per mine was keyed roughly to the size of its surface. Except for the PMA2, no more than 2% of the surface was taken up by the disks. Estimated mine surface areas and numbers of disks per sample are given in Table 2. The vials were kept at –4°C for storage and transport to the lab, where analysis was done. Analyses were completed within a week of sampling by gas chromatography with electron capture detection (Walsh and Ranney 1998).

In choosing to alter the procedure from that used in 1992, we attempted to circumvent some of the known

*Personal communication with P.J. Rodacy, Sandia National Laboratories, 1996.

Table 2. Mine characteristics and sampling parameters.

Mine	*Material*	*Area (cm²)*	*Number of disks*	*Percentage of area*
PMA1A-AP	PVC*	345	4	2
PMA2-AP	PS**	118	3	4
TMA5-AT	PS	2720	15	1
TMM1-AT	painted steel	2240	10	1

*Polyvinylchloride.
**Polystyrene.

problems alluded to above. We attempted to limit solvent penetration of casing materials by using methanol instead of more invasive solvents. Methanol is adequate for dissolving small amounts of explosives but not nearly as invasive of paints and plastics as acetone. No rubbing or wiping was done as before; the filter papers were simply emplaced, then removed with as little disturbance as possible. In view of the spatial heterogeneity of individual swabs observed in the 1992 study, we composited multiple disks to obtain a larger sample from each mine. This would give a better estimate of the total contamination present on each mine, while sacrificing information on smaller-scale distribution of contamination.

RESULTS AND DISCUSSION

One mine of each type was tested concurrently at CRREL for reproducibility of surface sampling. To do this, we placed several sets of disks on each mine and analyzed the replicate groups separately. Table 3 gives the means and standard deviations of replicate samples for the three major signature compounds using the above procedure. This would be a measure of the intra-mine/inter-sample variability. Generally, this produced numbers within about 10% of the means. For DNB and TNT on the TMM1, sampling variability was more than 60%, however.

Data for all the individual mines sampled at Fort Leonard Wood are not presented here, but may be made available at the discretion of the sponsor. Ranges, mean, and median surface concentrations of major signature components from this data set are given in Table 4. The frequency distributions expressed as percentage of mines with a given surface concentration are shown in Appendix B, Figures B1–B4. For a given mine type, the means and medians were generally similar, though the frequency distributions do not appear Gaussian in every case. RDX was found only on the PMA2 and is a component of the booster charge in this mine.

The question of whether the contamination recovered by this method is truly limited to the surface was addressed. One of each of the four mine types was sampled five times in rapid succession (i.e., within minutes) at two locations on the surface. The two disks were composited to form each sample and placed in 1 mL of acetonitrile for analysis, as before. The data are shown in Figure 1. Surface concentration measurements are clearly subject to experimental randomness but generally decreased with repeated sampling of the same spot. However, they don't go to "zero," which means that either the contamination is being replaced or it is not being efficiently recovered.

Environmental conditions at the time of sampling undoubtedly affect surface concentrations. The air inside the CRREL bunker was calm and the ambient temperature approximately 28°C. The conditions at Fort Leonard Wood were windy, and the ambient temperature was variable but generally higher. Surface samples were also taken at CRREL on a set of 12 mines at four carefully controlled temperatures ranging from 3 to 34°C, in conjunction with flux measurements. These data are scattered but suggest a rising trend in surface concentration with increasing temperature for all contaminants (Fig. 2). Wind might be expected to deplete surface concentrations relative to still air. According to mass transport theory, resistance to mass transfer decreases with wind speed, which means a higher flux from the surface with increasing wind speed (Thibodeaux 1979). Whether this causes depletion of surface concentrations, however, hasn't been determined. That would depend on the permeability of the material relative to the rate of desorption from the material.

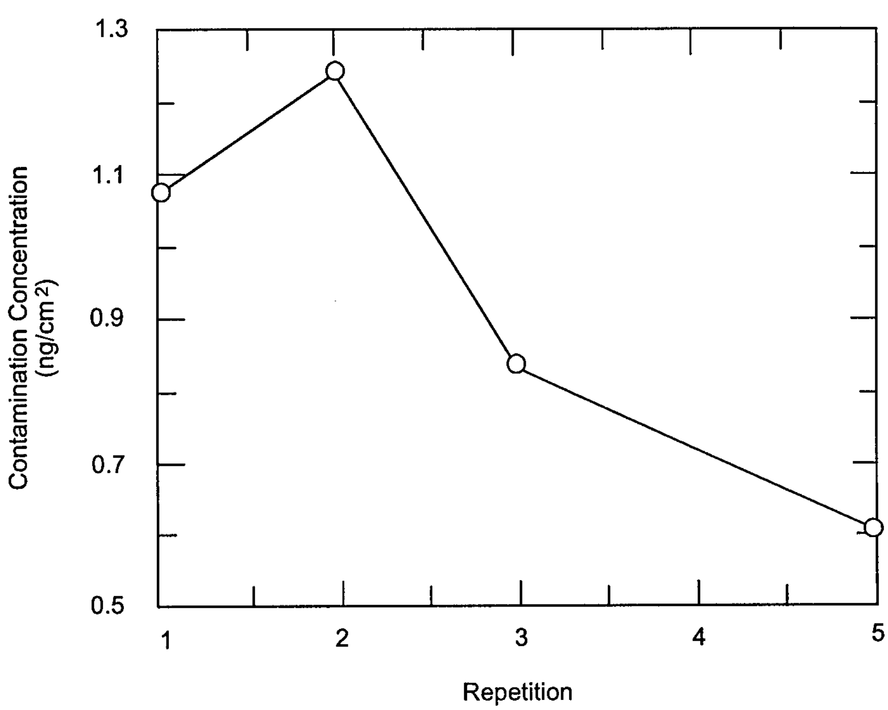
Under stagnant conditions in air, surface and bulk concentrations in the plastic may be near saturation (solubility). This is presumably the initial state of mines that have been boxed and stored in bunkers for many years prior to deployment and may persist when mines are deployed initially in dry soil. However, when liquid water comes in contact with a mine surface, these

Table 3. Mean concentrations (and standard deviations) of major surface contaminants found on mines sampled in the CRREL bunker at 28°C (ng/cm^2).

	1,3-DNB	*2,4-DNT*	*TNT*
PMA1A	2.92 (0.17)	1.87 (0.19)	1.55 (0.38)
PMA2	0.57 (0.02)	0.66 (0.03)	0.15 (0.07)
TMA5	1.50 (0.16)	8.01 (1.42)	6.25 (0.58)
TMM1	4.77 (2.99)	31.8 (2.75)	16.2 (11.0)

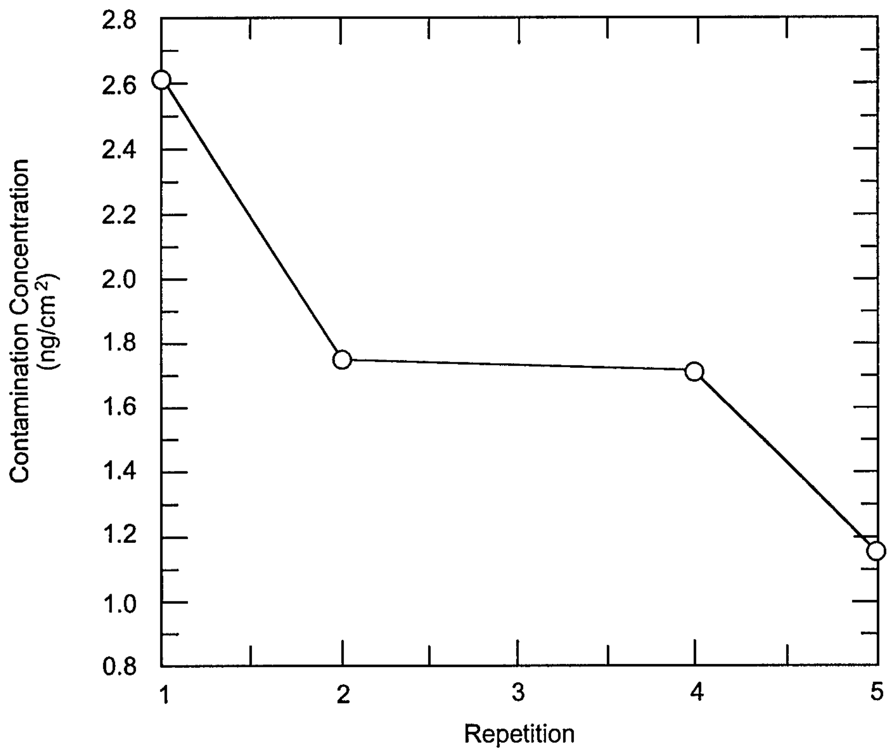
Table 4. Surface concentrations found on mines sampled at Fort Leonard Wood under ambient conditions (ng/cm²).

	PMA1A	*PMA2*	*TMA5*	*TMM1*
		1,3-DNB		
Min.	3.4	0.5	1.2	0.5
Max.	21.4	5.5	6.5	26.9
Mean	9.0	1.3	3.1	7.3
Median	8.6	1.0	2.7	5.8
		2,4-DNT		
Min.	1.6	0.3	1.4	2.6
Max.	16.7	2.0	23.3	29.4
Mean	4.8	0.9	6.1	11.0
Median	4.4	0.8	5.2	9.1
		TNT		
Min.	0.2	0.6	2.8	1.4
Max.	0.8	2.2	374	89.9
Mean	0.4	1.3	83.9	13.2
Median	0.4	1.2	52.1	5.9
		RDX		
Min.	—	0.5	—	—
Max.	—	2.2	—	—
Mean	—	1.2	—	—
Median	—	1.2	—	—

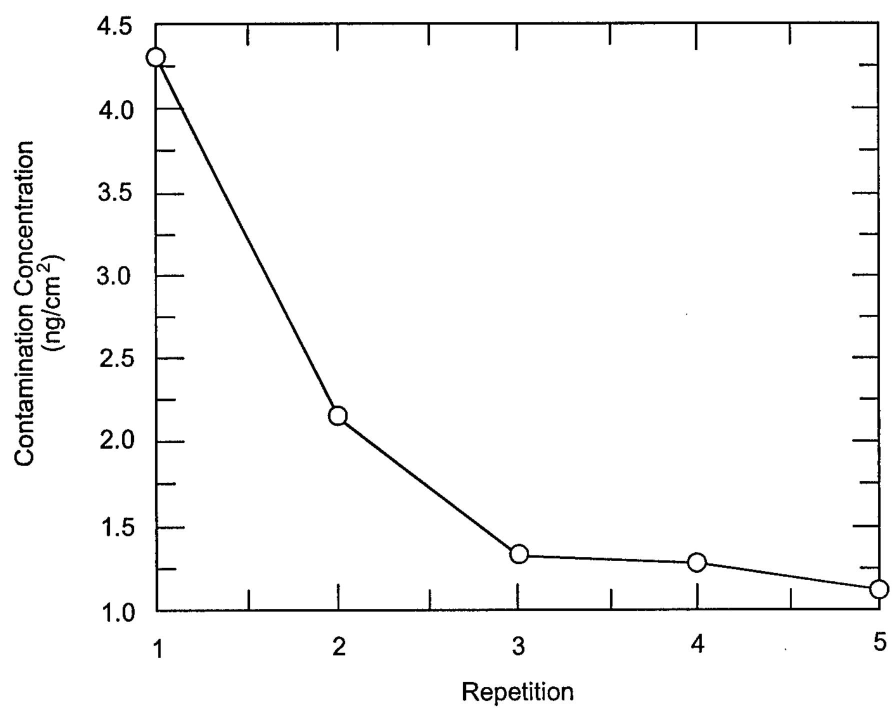


a. PMA1A.

Figure 1. Repeated surface sampling of landmines.

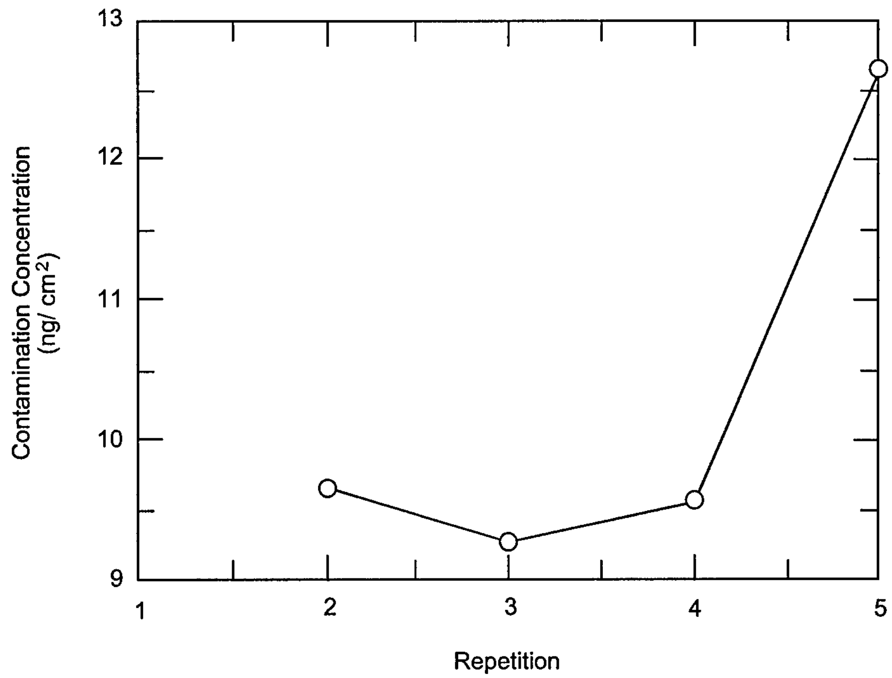


b. PMA2.



c. TMM1.

Figure 1 (cont'd).



d. TMA5.

Figure 1 (cont'd). Repeated surface sampling of landmines.

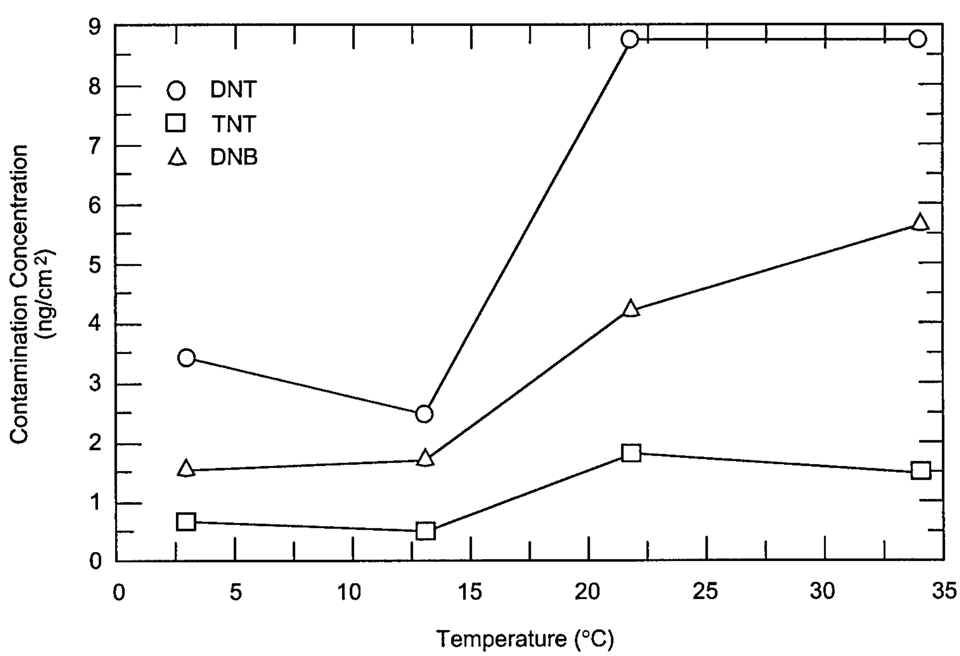


Figure 2. Temperature dependence of surface concentration.

concentrations will tend to be reduced by a more favorable partitioning into water. Observed decreases and redistribution of surface contamination after landmines have been buried tend to support this conclusion (field results, Fort Leonard Wood, 1999). Therefore, after deployment, mine surface concentrations (and fluxes) are expected to be under the influence of local wetting and drying cycles. This point will be discussed in more detail elsewhere (Leggett et al., in prep.; Leggett and Cragin, in prep.).

SUMMARY AND CONCLUSIONS

The earlier study, which included a greater range of mine types, found surface contamination ranging more widely than found here. The frequency distributions were highly skewed, approximately log-normally. Greater variability in the earlier study may also have been ascribable in part to researchers taking single swabs using an invasive solvent. With some exceptions, the current data ranged over approximately an order of magnitude within each mine type for each of the major signature components and were less skewed. Sampling of painted metal and plastic surfaces with solvent disks may have extracted contamination dissolved in the material as well as that on the surface. In any event, surface samples underestimate the size of the reservoir, which is three-dimensional. Surface contamination is renewable by contaminant vapors permeating through casing materials and by external contamination from other mines in proximity. External conditions such as temperature, wind, and moisture will influence surface concentrations. Liquid water, in particular, will quickly desorb surface contamination relative to still air, and will thus have a major influence on contaminant transport from buried mines under field conditions.

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APPENDIX A: Naval Ordnance Station SWIPES

Surface analyses of mines sampled at Naval Ordnance Station in 1992. One acetone-saturated cottom swab (5-cm^2 surface area) per mL acetonitrile, HPLC-UV analysis (254 nm).

Origin	*Mine*	*Type*	*Casing*	*Charge*	*Booster*	*TNT*	*RDX*
China	72	AP	Plastic/rubber	TNT/RDX(1/1)	RDX/WAX	95	5
Czechoslovakia	PT MI-K	AT	Metal	TNT		16	10
	"					12	7
	"					8	9
	"					7	7
	"					12	5
	"					21	7
	"					27	5
	PP MI-SR	AP	Steel/plastic	TNT		26	16
France	MB 51/55	AP	Steel	Picric acid ?		490	110
	"					540	26
	"					420	23
	"					96	10
Italy	SH 55	AT	Plastic	Comp B	RDX	27	200
	"					13	35
	"					11	23
	SB MV	AT	Plastic	Comp B	RDX-A3	<2	<2
	VS HCT2	AT	Plastic	Comp B		3	7
	VS-2.2	AT	Plastic	TNT/RDX		<2	68
	VS-1.6	AT	Plastic	TNT/RDX		<2	590
	VS 50	AP	Plastic	RDX		<2	30
	VALMARA 69	AP	Plastic	TNT/RDX	RDX	23	43
Soviet Union	OZM-72	AP	Steel	TNT	Tetryl	10	9
	"					8	100
	"					<2	37
	"					25	13
	"					150	27
	"					430	20
	"					430	23
US	M 16	AP	Metal	TNT	Tetryl	<2	<2
	"					<2	<2
	"					<2	<2
	"					<2	<2
	"					<2	<2
	"					<2	<2
	"					<2	<2
	"					22	<2
	M15	AT	Metal	Comp B		21	<2
	"					<2	<2
	"					23	<2
	"					<2	<2
	"					6	<2
	"					9	<2
	"					3	<2
	"					12	<2
Yugoslavia	PROM 1	AP	Steel	TNT		510	250
	TMA5	AT	Plastic	TNT	RDX	24	<2
	TMA4	AT	Plastic	TNT	Tetryl	127	<2
	"					39	<2
	"					23	<2
	TMA3	AT	None*	TNT		19,000	10,000

*Cast TNT.

APPENDIX A *(cont'd)*: Naval Ordnance Station SWIPES

Concentration			
2,4-DNT	*2-4-ADNT*	*Tetryl*	
30			
4	2		
	5		
260	23		
260	23		
51		18	
7	6		
4	3		
4	2		
1			
5			
4	4		
	6		
3	5		
3	3		
3	8		
2	6		
4			
4			
3			
	14		
6		9	
36	15	6	
40			
570		4	
130			
70			
5000			1400 HMX

*Cast TNT.

APPENDIX B: FREQUENCY DISTRIBUTION OF SURFACE SAMPLES

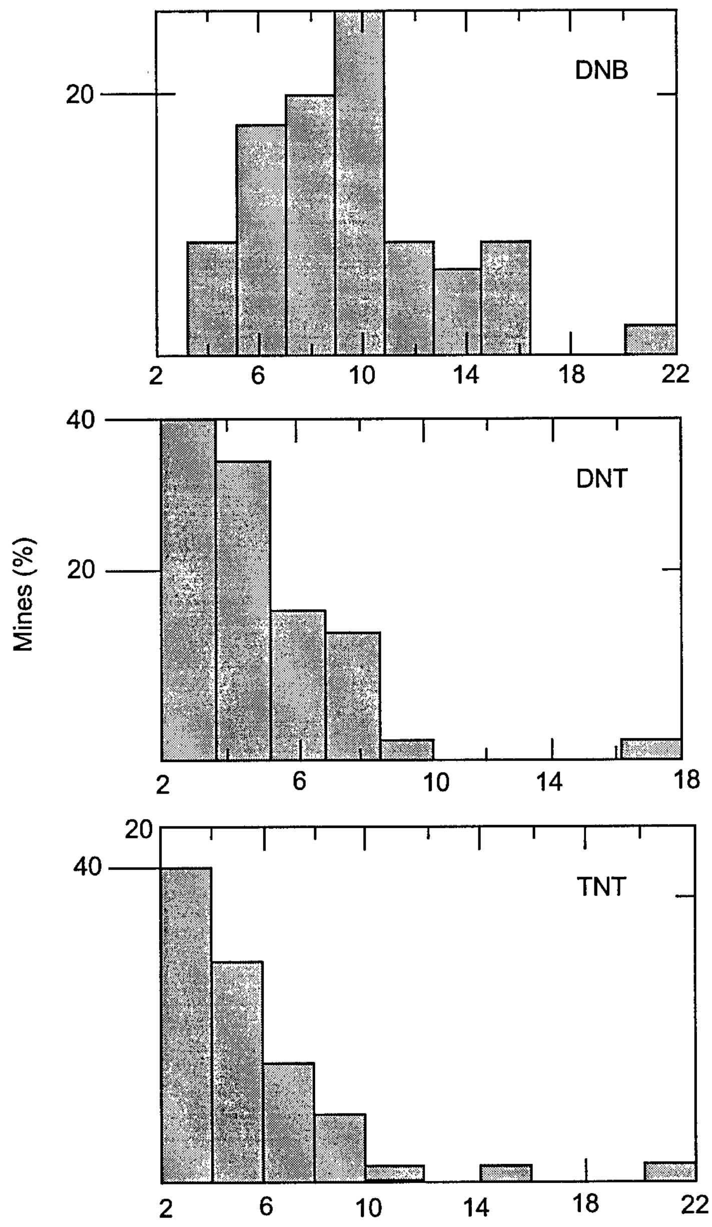

Figure B1. PMA1A surface concentrations (ng/cm^2).

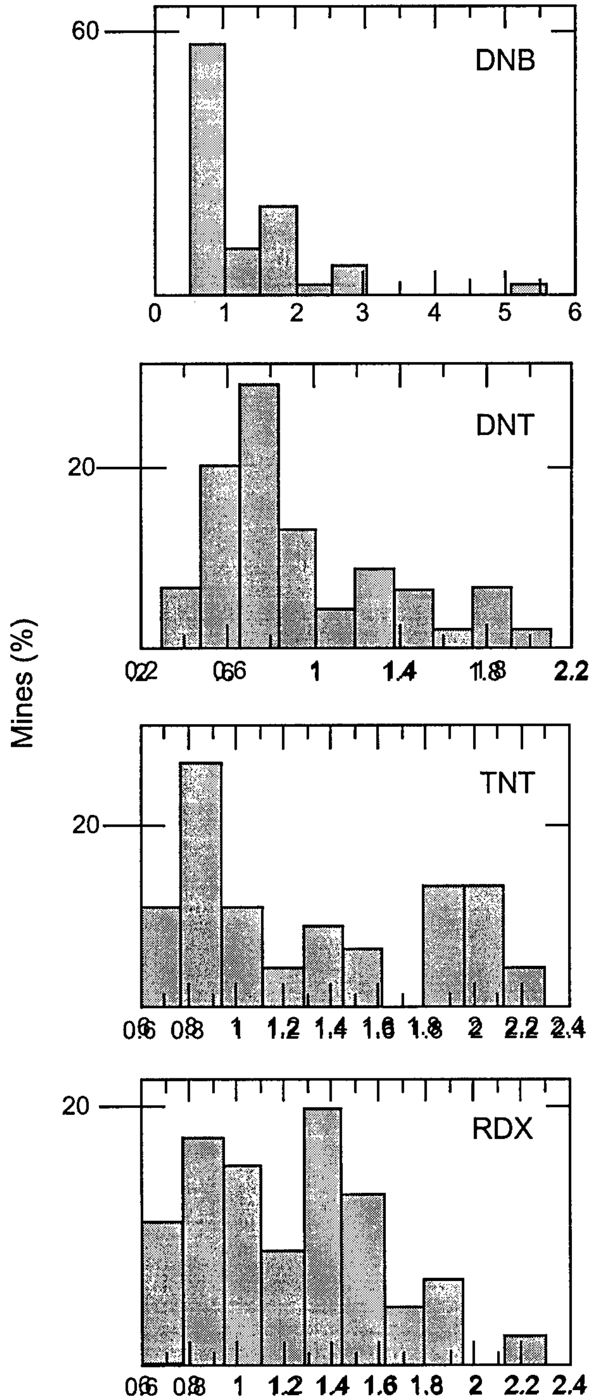

Figure B2. PMA2 surface concentrations (ng/cm²).

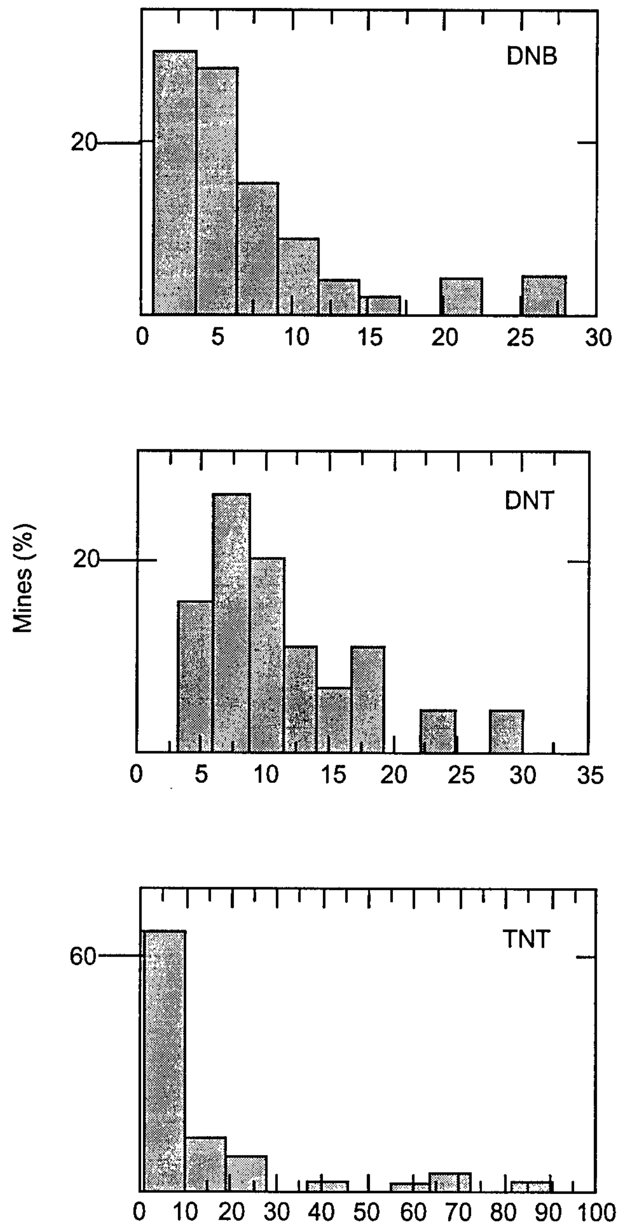

Figure B3. TMM1 surface concentrations (ng/cm^2).

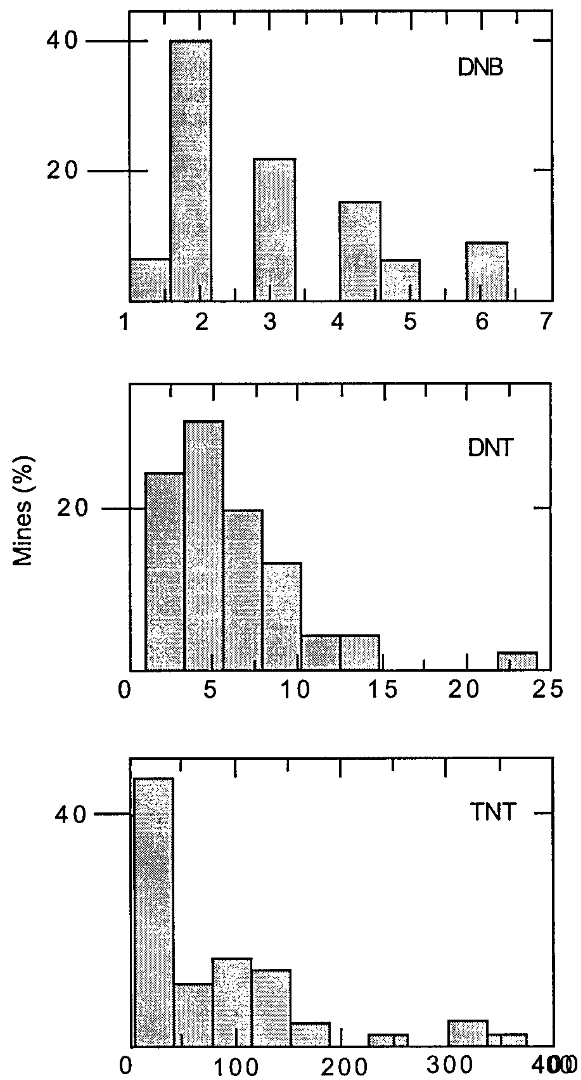

Figure B4. TMA5 surface concentrations (ng/cm^2).

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14. ABSTRACT

It has been known for years that landmines are contaminated on their surfaces by explosive compounds. Subsequently, it was shown that TNT vapor-contaminated surfaces outgas at a significant rate. This has encouraged the quest for chemical systems for buried mine detection. This report documents a recent study of four types of mines obtained from former Yugoslavian inventories. In addition it presents the results of a study of 18 foreign and domestic types of landmines examined in 1992. Contamination was removed from known areas of the surface by solvent-soaked swabs and several swabs pooled for each mine. Surface concentrations ranged from 1 to 400 ng/cm^2 over all mine types, but was generally less variable within each type. There appears to be an increase of surface contamination with temperature, though this could be due to increased flux rather than increased concentration. Sampling mine casings using swabs may recover more than is truly on the surface, because contamination is regenerated from within material by diffusive permeation. Similarly, single swabs recover this subsurface contamination inefficiently, as sequential sampling of the same area continues to extract contamination. For this reason, these measurements under-represent source size. Surface concentrations are influenced by conditions external to the mines, and after deployment will be influenced by soil moisture.

15. SUBJECT TERMS

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